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(54) Title: OPTICAL RECORDING WITH NEAR-INFRARED DYES TO EFFECT BLEACHING

(57) Abstract

The present invention relates to an optical recording element comprising a near-infrared absorbing dye, and acid-photo-generating compound, and an optical near-ultraviolet absorbing sensitizer which bleaches upon exposure to either near-infrared or near-ultraviolet radiation. A method of optical recording with this element is also disclosed.

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- 1 -

OPTICAL RECORDING WITH NEAR-INFRARED  
DYES TO EFFECT BLEACHING

FIELD OF THE INVENTION

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This invention relates to optical recording elements containing near-infrared dyes and acid photogenerating compounds. Recording is accomplished by bleaching of the recording layer upon exposure to near-infrared or near-ultraviolet radiation.

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DESCRIPTION OF THE PRIOR ART

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This invention relates to imaging and recording methods that employ near-infrared light sources to write and/or read information, particularly in the form of digitized information. For the purposes of this invention, near-infrared radiation is defined as radiation with a wavelength between about 700 to 1,000 nm. Many typical applications of near-infrared lasers feature optical disks upon which digitized information is written and subsequently read by diode lasers of differing power or wavelength.

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These processes often involve "ablation", or "pitting", of the optical disk recording material.

Ablation or pitting processes involve the actual removal of portions of the recording medium with a laser. The laser, by removing minute amounts of the recording medium bit by bit, records information on the disk.

25

This information may later be read by scanning the disk with a laser of relatively lower power and/or wavelength. Wherever ablated areas are encountered, the laser beam is deflected. This deflection is detected and converted to an electrical signal. Ablation or

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pitting techniques have been discussed in the patent and other literature, examples are disclosed in U.S. Patent

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No. 4,460,665 to Kunikane et al., U.S. Patent  
No. 4,546,444 to Bell et al. and others.

Ablative techniques have many drawbacks. For example, as a consequence of ablation, material may also 5 be ejected from the substrate. This material can contaminate the process. Additionally, it is difficult to mass-produce disks that have been recorded using ablative techniques. Information must be recorded one bit at a time, which is time-consuming and costly.

10 Recording pits may also be formed by conventional methods such as injection molding or press forming. These processes require expensive precision molding machines. Other disadvantages include limitations on the make-up of molding materials, and clogging of the print-transferring 15 stamps used in production.

Certain non-ablative techniques have also been described for optical recording. U.S. Patent No. 4,707,425 to Sasagawa et al. and U.S. Patent No. 4,707,430 to Ozawa et al. disclose a non-ablative 20 technique of optical recording.

In Sasagawa et al., the recording medium comprises a substance which has an absorption maximum in the near-infrared range of the electromagnetic spectrum and loses or diminishes its power to absorb visible or 25 near-infrared radiation when exposed to ultraviolet radiation, x-rays, electron beams, or ion beams. The information is recorded by exposing the recording medium to ultraviolet radiation, x-rays, electron or ion beams and read by detecting changes in the medium's ability to 30 absorb near-infrared radiation.

In Ozawa et al., a recording medium comprising an organometallic complex having an absorption maximum in the near-infrared range, a resinous binder, and a sensitizer capable of generating radicals upon exposure to 35 ultraviolet radiation. Information is recorded by exposure to ultraviolet radiation which, like Sasagawa

WO 93/06597

- 3 -

et al., diminishes the medium's ability to absorb visible and near-infrared radiation in the exposed areas.

The optical recording media disclosed in Sasagawa et al. and Ozawa et al. may not, however, be recorded upon 5 with near-infrared radiation.

SUMMARY OF THE INVENTION

The present invention relates to an optical 10 recording element comprising a reflective substrate and a recording layer comprising a near-infrared radiation absorbing dye that undergoes bleaching upon exposure to near-infrared radiation, and an acid photogenerating compound. The near-infrared absorbing dye may also be 15 bleached upon exposure to near-ultraviolet radiation. For the purposes of this invention, near-ultraviolet radiation is defined as radiation with a wavelength between about 250-400 nm. A near-ultraviolet absorbing sensitizer may also be added to the recording layer of the element of the 20 present invention to further facilitate bleaching upon exposure to near-ultraviolet radiation. Thus, the recording element of the present invention allows optical recording with either near-infrared or near-ultraviolet radiation without ablation or pit formation.

25 The present invention also provides a method of optical recording that utilizes the above-described optical recording element. This method comprises the steps of providing the above-described optical recording element, and exposing the element with near-infrared or 30 near-ultraviolet radiation. The recorded information may be read by exposure to near-infrared radiation to detect any color density or hue shift.

The optical recording element of the present invention has the advantages of recording concurrent with 5 exposure without the disadvantages of ablation techniques. Information may be recorded in one exposure

- 4 -

without any additional steps due to the bleaching of the recording medium.

The invention is unique in that information may be recorded on the element utilizing either near-infrared or near-ultraviolet radiation. In either case, the information may be read back using near-infrared radiation. Furthermore, these compositions, when used in conjunction with a photomask containing digitized information, allow for all the digitized information to be recorded in a single blanket exposure of near-ultraviolet radiation. No post-exposure development or processing is required. This method of mass replication of the optically recorded information is therefore quick and cost-efficient.

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#### DETAILED DESCRIPTION OF THE INVENTION

As noted above, this invention relates to optical recording elements containing near-infrared absorbing dyes 20 and acid-photogenerating compounds. Recording is accomplished by a bleaching upon exposure to activating radiation. Recording is accomplished without the use of ablation techniques.

In the optical recording element of the present 25 invention, the recording layer comprises a dye with an absorption maximum in the near-infrared wavelength range of about 700 to 1000 nm, and an acid-photogenerating compound. A near-ultraviolet absorbing sensitizer may also be added to facilitate the absorption of 30 near-ultraviolet radiation. As a result of this combination, the near-infrared absorbance of the dye is diminished in whole or in part upon exposure of the element to near-infrared or near-ultraviolet radiation.

The recording layer of the optical recording 35 element of the present invention is employed as a separate thin layer coated on a suitable substrate. This substrate

acts as a support for the recording layer of the element.

The substrate may be chosen from a variety of solid materials, either flexible or rigid. Suitable substrate materials include glass, quartz, ceramics, 5 paper, plate-like or foil-like metal, methacrylates, methacrylic acid ester copolymers, polycarbonates, vinyl chlorides, styrene copolymers, polyesters, acrylonitrile-styrenes, and cellulose acetates. Preferred substrate materials include methyl methacrylate.

10 If the substrate of the recording element of the present invention does not have reflective characteristics, a reflective layer is typically added. The reflective layer is preferably located between the substrate and the recording layer. Suitable materials for 15 the reflective layer include aluminum, copper, chromium, gold, and rhodium. The thickness of the light reflecting layer should be sufficient to reflect a significant amount of the recording radiation.

Leveling and/or priming layers may also be 20 applied to the substrate before application of the reflective coating and/or the recording layer. The reflective material itself may constitute the substrate if it is self-sustaining and optically smooth.

The recording layer of the present invention is 25 normally coated on the substrate. Suitable methods of coating include handcoating, dipcoating, spincoating, and webcoating.

The recording layer of the present invention contains a near-infrared absorbing dye. Many 30 near-infrared absorbing dyes are known to exist. However, only dyes that are unreactive and unbleached upon combination with an acid-photogenerating compound before exposure, but bleach upon exposure, to activating radiation are practically useful. Examples of useful 35 near-infrared absorbing dyes include nitroso compounds or a metal complex salt thereof, methine dyes, cyanine dyes,

merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, hemicyanine dyes, styryl dyes, hemioxonol dyes, squaryllium dyes, thiol metal complex salts (including nickel, cobalt, platinum, palladium 5 complex salts), phthalocyanine dyes, triallylmethane dyes, triphenylmethane dyes, iminium dyes, diimmonium dyes, naphthoquinone dyes, and anthroquinone dyes.

Preferred near-infrared dyes include those of the cyanine class. Particularly useful cyanine dyes include 10 3,3'-diethylthiatricarbocyanine iodide ("DTTC") and 1,1'-diethyl-4,4'-carbocyanine iodide (cryptocyanine).

The near-infrared absorbing dye should be present in a concentration sufficient to strongly absorb the activating radiation. The concentration of the 15 near-infrared absorbing dye will vary depending upon the acid-photogenerating compound used, the thickness of the recording layer, and the near-infrared absorbing dye used. Generally, the concentration of the near-infrared absorbing dye will be in the range of 0.1 to 10 percent by 20 weight of the recording layer

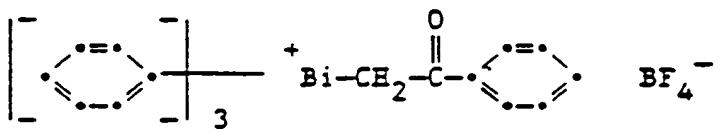
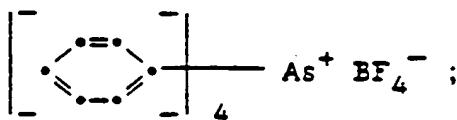
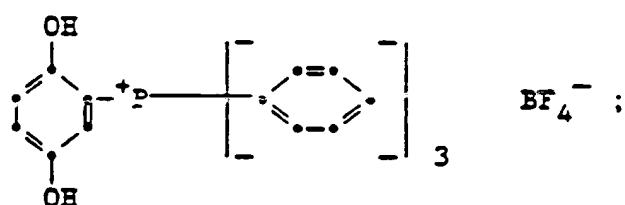
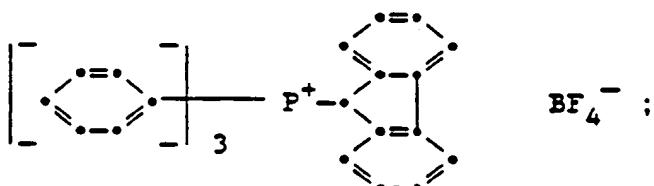
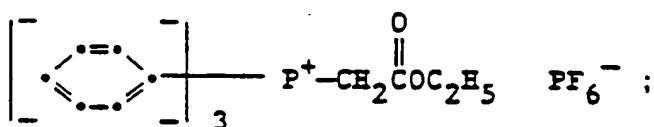
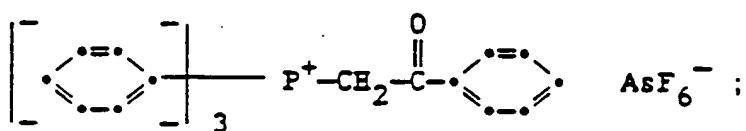
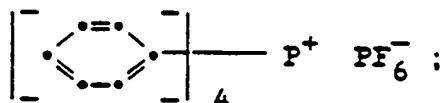
Although generally, any compound which generates an acid upon near-infrared radiation exposure may be useful, the acid-photogenerating compound of the element of the present invention should be selected to leave the 25 near-infrared absorbing dye unbleached before the element is exposed to activating radiation. Additionally, the acid-photogenerating compound should not absorb strongly in the visible region of the spectrum unless this absorption is ineffective in bleaching the near-infrared 30 absorbing dye. Although there are many known acid photogenerators useful with ultraviolet and visible radiation, the utility of their exposure with near-infrared radiation is unpredictable. Potentially useful aromatic onium salt acid photogenerators are 35 disclosed in U.S. Patent Nos. 4,661,429, 4,081,276, 4,529,490, 4,216,288, 4,058,401, 4,069,055, 3,981,897, and

- 7 -

2,807,648 which are hereby incorporated by reference. Such aromatic onium salts include Group Va, Group VIa, and Group VIIa elements. The ability of triarylselenonium salts and triarylsulfonium salts to produce protons upon 5 exposure to ultraviolet and visible light is also described in detail in "UV Curing, Science and Technology", Technology Marketing Corporation, Publishing Division, 1978.

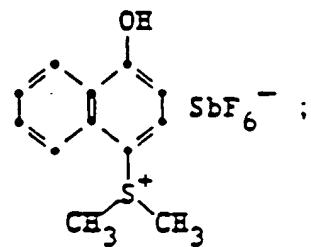
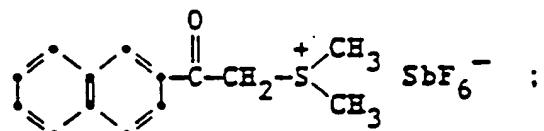
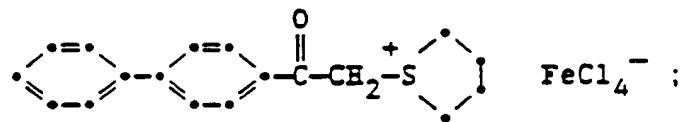
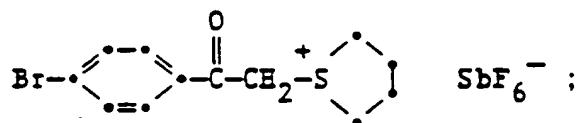
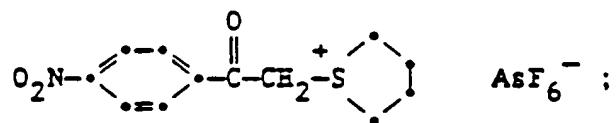
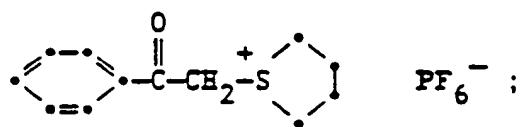
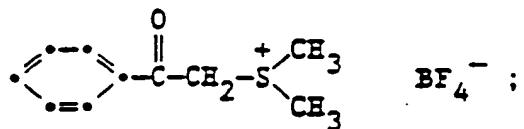
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A representative portion of useful Group Va  
onium salts are:

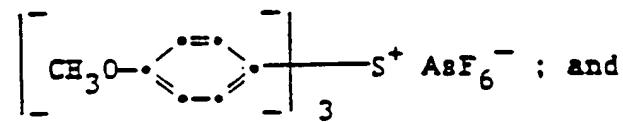
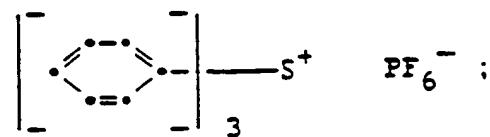
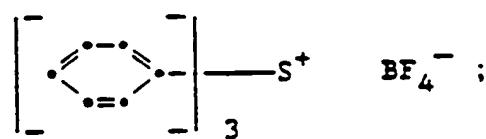
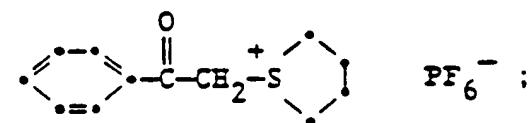
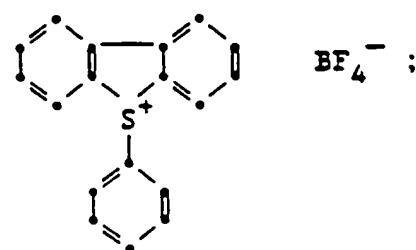
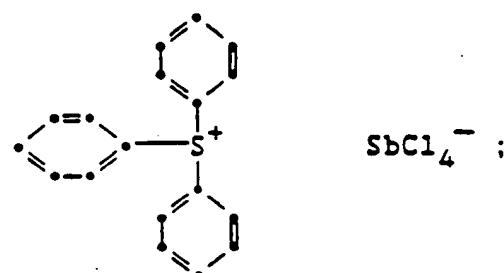
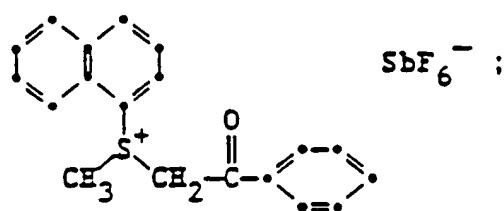


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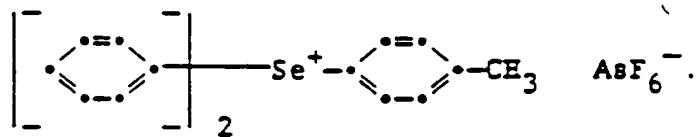
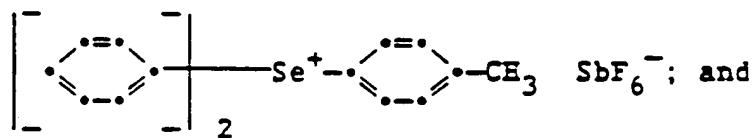
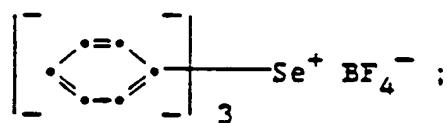
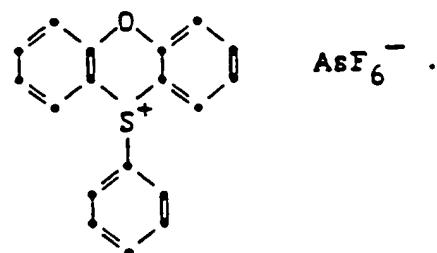
A representative portion of useful Group VIA  
onium salts, including sulfonium and selenonium salts,  
are:



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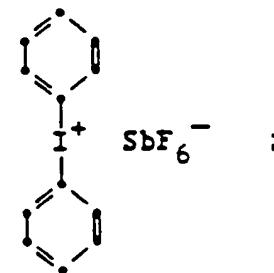
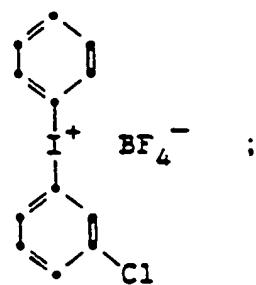
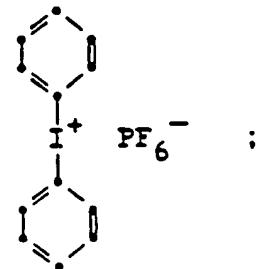
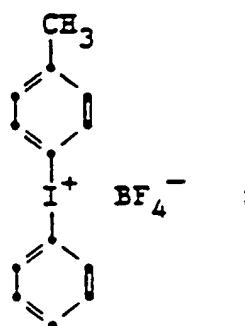


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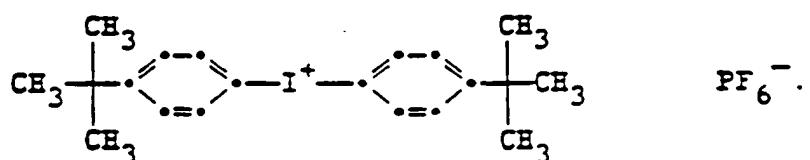
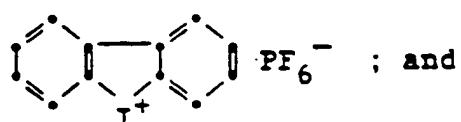
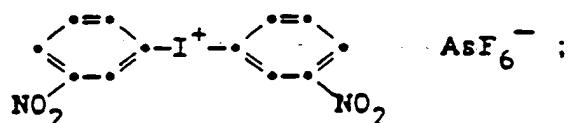
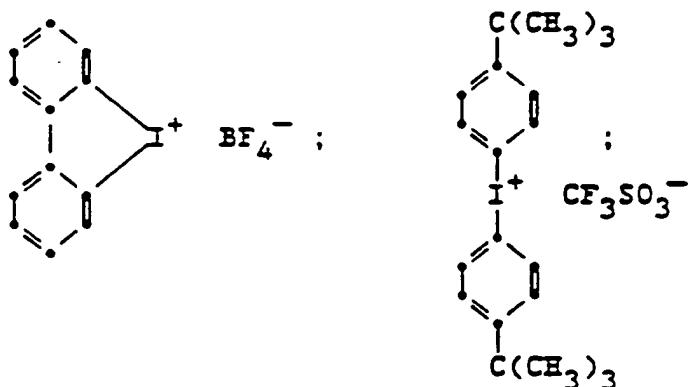


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A representative portion of the useful  
Group VIIa onium salts, including iodonium salts, are  
the following:



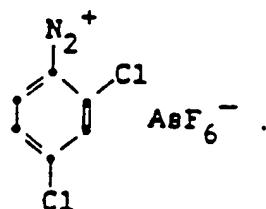
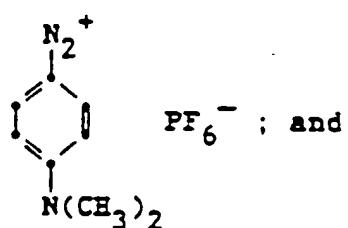
- 13 -



- 14 -

Also useful as acid photogenerating compounds are:

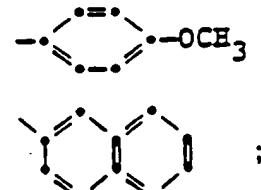
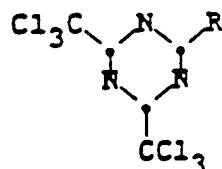
1. Aryldiazonium salts such as disclosed in U.S. Patent Nos. 3,205,157; 3,711,396; 3,816,281; 5 3,817,840 and 3,829,369. The following salts are representative:



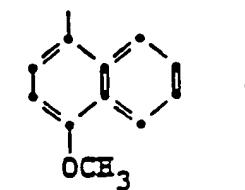
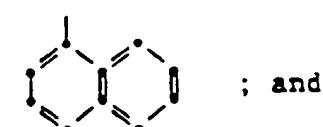
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2. 6-Substituted-2,4-bis(trichloromethyl)-5-triazines such as disclosed in British Patent No. 1,388,492. The following compounds are representative:

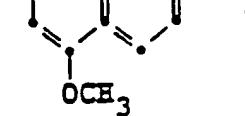
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A particularly preferred class of acid photogenerators are the diaryliodonium salts and triarylsulfonium salts. For example, di-(4-t-butylphenyl)iodonium trifluoromethanesulfonate and triphenylsulfonium trifluoromethanesulfonate have shown particular utility.

The concentration of the acid photogenerating compound should be sufficient to substantially or completely bleach the near-infrared absorbing dye when the element is exposed to an amount of actinic radiation normally used in the recording process. This concentration will generally be in the range of 1 to 50 percent by weight of recording layer.

Information may also be recorded on the element of the present invention using near-ultraviolet radiation. The above-described combination of a near-infrared sensitive dye and a near-ultraviolet absorbing acid-photogenerating compound may itself

- 16 -

absorbing acid-photogenerating compound may itself bleach upon exposure to near-ultraviolet radiation. However, the addition of a near-ultraviolet absorbing sensitizer will accelerate this process. The amount of 5 sensitizer used varies widely, depending on the type of near-infrared absorbing dye and acid-photogenerating compound used, the thickness of the recording layer, and the particular sensitizer used. Generally, the sensitizer may be present in an amount of up to about 10 10 percent by weight of the recording layer.

Iodonium salt acid-photogenerators may be sensitized with ketones such as xanthones, indandiones, indanones, thioxanthones, acetophenones, benzophenones, or other aromatic compounds such as anthracenes, 15 dialkoxyanthracenes, perylenes, phenothiazines, etc. Triarylsulfonium salt acid photogenerators may be sensitized by aromatic hydrocarbons, anthracenes, perylenes, pyrenes, and phenothiazines.

Near-ultraviolet absorbing sensitizers of the 20 anthracene family are especially preferred when used in combination with the preferred onium salts described above. 9,10-Disubstituted anthracenes, such as 9,10-diethoxyanthracene, are particularly useful.

The recording layer of the optical recording 25 element of the present invention will typically contain a film-forming, polymeric binder to facilitate the coating of the recording layer upon a suitable substrate. Useful film-forming binders include the polycarbonates, polyesters, styrenics, methacrylic ester 30 copolymers, vinyl chlorides, cellulose derivatives (such as cellulose acetate, cellulose butyrate and cellulose nitrate), alkyds, polyurethanes, styrene-butadiene copolymers, silicone resins, styrene-alkyd resins; soya-alkyd resins, poly(vinyl chloride), poly(vinylidene 35 chloride), vinylidene chloride, acrylonitrile copolymers, poly(vinyl acetate), vinyl acetate, vinyl

chloride copolymers, poly(vinyl acetals) (such as poly(vinyl butyral)), polyacrylic esters (such as poly(methyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate), etc.), polystyrene, 5 nitrated polystyrene, poly(vinylphenol), polymethylstyrene, and isobutylene polymers. A particularly preferred class of binders are aromatic esters of polyvinyl alcohol polymers and copolymers. Examples are disclosed in United States Patent 10 Application Serial No. 509,119.

The recording layer of the element should have a thickness in the range of 0.1 to 20  $\mu\text{m}$ . A thickness of 0.1 to 5.0  $\mu\text{m}$  is preferred. The layer should also be durable, smooth, and free from coating defects such as 15 pinholes or reticulation.

This invention also provides a method of optical recording that utilizes the above-described optical recording element. Information is recorded on the optical recording element, which comprises the 20 recording layer described above, by exposing it to actinic radiation.

In one embodiment of this invention, a recording element featuring a recording layer comprising a near-infrared absorbing dye and an 25 acid-photogenerating compound is exposed to near-infrared radiation. In the areas exposed to near-infrared radiation from a near-infrared laser the near-infrared absorbing dye undergoes bleaching. Signals are recorded because absorption of wavelengths 30 in the range of 700-1000 nm, which corresponds to the wavelengths of the reading laser beam, is diminished significantly compared to the unexposed areas. Reading of the recorded information is accomplished with lower power near-infrared exposures that detect the 35 differential absorption between the exposed and unexposed areas. These absorption characteristics are

- 18 -

then converted to electrical signals that may be transduced to reproduce images, voice, or sound.

Recording may be accomplished using various sources of near-infrared radiation. Suitable sources of 5 near-infrared radiation include diode lasers. A digital pattern may be formed on the optical element by narrowing a near-infrared laser beam to a spot beam and scanning the recording layer in a pattern corresponding to the signals to be recorded. Scanning may be 10 accomplished by moving either the laser or the element or both.

In another embodiment of this invention, recording is accomplished using near-ultraviolet radiation. Suitable sources of near-ultraviolet 15 radiation include mercury arc lamps and ultraviolet lasers. Although a recording element with just a near-infrared absorbing dye and an acid photogenerator may bleach upon exposure to near-ultraviolet radiation, it is preferred to add a near-ultraviolet absorbing 20 sensitizer to facilitate such bleaching.

Recording using near-ultraviolet radiation may be accomplished through scanning exposures as described above. Preferably, blanket exposures through a photomask pattern of digitized information will record 25 the whole of the information in a single exposure.

Reading is accomplished in this procedure as described above, using a low power near-infrared laser to detect the differential near-infrared absorption characteristics of the optical recording element of the 30 present invention.

Therefore, the recording element of the present invention may be bleached and recorded with either near-infrared or near-ultraviolet radiation and, in either case, read with near-infrared radiation. None of 35 the disadvantages associated with ablation techniques exist. The element and method of the present invention

- 19 -

provide an efficient, low-cost procedure for recording and replicating information on optical recording media.

The invention is further illustrated by the following examples.

5

#### EXAMPLES

In the examples which follow, the preparation and characterization of representative materials and formulations are described. These examples are provided to illustrate the usefulness of the compositions of the 10 present invention and are by no means intended to exclude the use of other compositions which fall within the above disclosure.

##### Example 1

15 A thin film comprising 25 weight percent ("wt%") di-(t-butylphenyl)iodonium trifluoromethanesulfonate ("ITf") as the acid-photogenerator, 5 wt% 9,10-diethoxyanthracene ("DEA") as the near-ultraviolet sensitizer, 3 wt% 20 3,3'-diethylthiatricarbocyanine iodide ("DTTC") as the near-infrared dye, and 67 wt% poly(vinyl benzoate-co-vinylacetate) in a 88/12 molar ratio ("PVBzAc") as a polymeric binder, is coated over a transparent support of polyethylene terephthalate by 25 machine coating. The film appears pale green as-coated, and photomicroscopy of a cross-section shows the film to be 2.8  $\mu\text{m}$  thick. Spectroscopy shows strong absorption from 600 to 850 nm, which displays a maximum absorption at 781 nm with an optical density ("OD") of greater than 30 2.5. The film also displays several absorption maxima between 350 and 410 nm due to the near-UV sensitizer (DEA).

A portion of the film was exposed to near-ultraviolet light from a 500W mercury arc source 35 for 90 seconds, for a total exposure of about 2.7 joules/cm<sup>2</sup>. The pale green color was completely faded,

- 20 -

and spectroscopy showed an OD of less than 0.10 at wavelengths greater than 600 nm.

Another portion of the film was exposed on a breadboard equipped with a 200 mw near-infrared laser diode (827 nm output), and the output beam focused to a 30 $\mu$ m spot. The breadboard consists of a rotating drum, upon which the film is mounted, and a translation stage which moves the laser beam along the drum length. The drum rotation, the laser beam location, and the laser beam intensity are all controlled by an IBM-AT computer. The drum was rotated at a speed of 120 rpm, and the film was exposed to an electronically generated graduated exposure consisting of 11 exposure steps. The line spacing (distance between scan lines in the continuous tone step-wedge) was 20  $\mu$ m, and the maximum intensity was about 100 mw with an exposure time of about 30  $\mu$ sec/pixel. Within one-half hour after exposure, the sample was mounted and tested on a separate linear breadboard.

20 The step-wedge thus produced appeared rust-colored in the areas of maximum exposure, and six density steps in the wedge were clearly visible. Spectroscopy of an area which had received maximum exposure revealed an OD of 0.41 at 780 nm compared to an 25 OD of greater than 2.5 at 780 nm of an adjacent, unexposed area.

This example shows that significant bleaching of the infrared absorption occurs with either near-infrared or near-ultraviolet exposure.

30

Example 2

A film similar to that described in Example 1 is also coated, except that no near-ultraviolet absorbing sensitizer is added. The ratios of the 35 components are 25 wt% ITf, 3 wt% DTTC, and 72 wt% PVBzAc. The thickness of the recording layer is 7.4  $\mu$ m,

- 21 -

and the OD at 780 nm is greater than 4.0. After exposure to near-ultraviolet radiation, as described in Example 1, the OD at 780 nm is 1.42. A second maximum is observed with an OD of 0.46 at 545 nm. These results 5 indicate that although bleaching of the near-infrared absorption will occur without the addition of a near-ultraviolet sensitizer, a near-ultraviolet sensitizer will allow for more efficient bleaching with near-ultraviolet radiation.

10 A second portion of this film is exposed to near-infrared radiation on a breadboard in the same manner as described in Example 1. Six clear density steps are visible. The areas which receive maximum exposure are rust-colored, and spectroscopy of these 15 areas reveals absorption maxima at 545 nm (OD of 0.43) and 775 nm (OD of 0.63). These results indicate that the near-ultraviolet absorbing sensitizer is not required for bleaching concurrent with near-infrared exposure.

20

Example 3

Another film is coated in the same manner as described in Example 1, except that no acid-photogenerating compound is included. The weight 25 ratios of the components are 5 % DEA, 3 % DTTC, and 92 % PVBzAc. The film is 3.2  $\mu$ m thick and displayed an absorption maximum at 785 nm (OD = 1.29). After exposure with near-ultraviolet radiation, as described above, the OD at 785 nm is found to be 0.83.

30 Near-infrared exposure on the LTI breadboard results in no visible change in density or hue. Spectroscopy of an area which had received maximum exposure shows virtually no difference when compared to an adjacent, unexposed area. Thus, for significant bleaching to occur with 35 either near-infrared or near-ultraviolet radiation, an acid-photogenerating compound must be present.

Example 4

Several film samples are coated as described in Example 1, except that the acid-photogenerating compounds are varied. Accompanying Table I lists the 5 varying acid-photogenerating compounds and their respective bleaching efficiency as a function of both near-ultraviolet and near-infrared exposure. Film thicknesses range between 8 and 11  $\mu\text{m}$ . The samples are exposed in the same manner as described in Example 1. 10 In Table I, bleaching efficiency is defined as:

$$1 - \left[ \frac{\text{OD} @ 700 \text{ nm (exposed)}}{\text{OD} @ 700 \text{ nm (unexposed)}} \right]$$

15 The OD at 700 nm was chosen as the reference point because many of the films display ODs that are off scale at the 780 nm absorption maximum.

- 23 -

TABLE I

5	ACID-GENERATOR	BLEACHING-EFFICIENCY	NEAR-UV	NEAR-IR
10	di-(4-t-butylphenyl)iodonium trifluoromethanesulfonate		0.80	0.82
15	di-(4-t-butylphenyl)iodonium hexafluorophosphate		0.91	0.76
20	di-(4-t-butylphenyl)iodonium p-toluenesulfonate	0.36	0.43	
25	di-(4-t-butylphenyl)iodonium perfluorobutyrate	0.51	0.33	
	triphenylsulfonium hexafluorophosphate	0.92	0.14	
	triphenylsulfonium hexafluorophosphate	0.83	0.13	
	None (control)	0.34	0.15	

30 Table I illustrates the effectiveness of various acid-photogenerating compounds when used in the optical recording element of the present invention. The higher the bleaching efficiency value (maximum bleaching efficiency is 1.0) the more effective the 35 acid-photogenerating compound.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the 40 art without departing from the spirit and scope of the invention which is defined by the following claims.

- 24 -

WHAT IS CLAIMED:

1. An optical recording element comprising:
  - a substrate and
  - 5 a recording layer coated on said substrate comprising:
    - a dye which undergoes a color density or hue shift upon exposure of said recording layer with near-infrared radiation and
    - 10 an acid-photogenerating compound.
2. The element of claim 1, wherein said dye is chosen from the group consisting of cyanine dyes.
3. The element of claim 2, wherein said cyanine dye is chosen from the group consisting of
  - 15 3,3'-diethylthiatricarbocyanine, and
  - 1,1'-diethyl-4,4'-carbocyanine iodide.
4. The element of claim 1, wherein said acid photogenerating compound is an aromatic onium salt selected from the group consisting of aryl halonium
  - 20 salts, aryl phosphonium salts, aryl arsenonium salts, aryl sulfonium salts, aryl selenonium salts, aryl diazonium salts, and mixtures thereof.
5. The element of claim 4, wherein said onium salt is chosen from the group consisting of
  - 25 triarylsulfonium salts and diaryliodonium salts.
6. The element of claim 5, wherein said onium salt is chosen from the group consisting of triphenylsulfonium hexafluorophosphate, di-(4-t-butylphenyl)iodonium hexafluorophosphate,
  - 30 triphenylsulfonium trifluoromethanesulfonate, and
  - di-(4-t-butylphenyl)iodonium trifluoromethanesulfonate,
7. The element of claim 1 further comprising:
  - a polymeric binder.
8. The element of claim 7, wherein said
  - 35 polymeric binder is chosen from a group consisting of polycarbonates, polyesters, styrenics, polyimides,

- 25 -

poly(methacrylates) and poly(acrylates).

9. The element of claim 7 further comprising:  
a near-ultraviolet absorbing sensitizer

10. The element of claim 9, wherein said  
5 near-ultraviolet absorbing sensitizer is chosen from the  
group consisting of xanthones, indandiones, indanones,  
throxanthones, acetophenones, benzophenones,  
anthracenes, dialkoxyanthracenes, perylenes,  
phenothiazines, and pyrenes.

11. The element of claim 1 further comprising:  
10 a near-ultraviolet absorbing sensitizer.

12. The element of claim 11, wherein said  
near-ultraviolet absorbing sensitizer is chosen from the  
group consisting of xanthones, indandiones, indanones,  
15 throxanthones, acetophenones, benzophenones,  
anthracenes, dialkoxyanthracenes, perylenes,  
phenothiazines, and pyrenes.

13. The element of claim 7, wherein the  
concentration of said near-infrared absorbing dye is in  
20 the range of 0.1 to 10 weight percent, the concentration  
of said acid photogenerating compound is in the range 1  
to 50 weight percent, and the concentration of said  
binder is 40 to 98.9 weight percent.

14. A method for optically recording  
25 information which comprises the steps of:  
providing an optical recording element  
comprising:

a substrate and  
a recording layer coated on said substrate

30 comprising:

a dye which undergoes a color density  
or hue shift following exposure of said  
recording layer with near-infrared  
radiation and

35 an acid photogenerating compound;  
exposing said recording element in desired

- 26 -

locations with activating radiation to effect a color density or hue shift in said recording layer suitable for subsequent reading with near-infrared radiation.

15. The method of claim 14, wherein said  
5 exposing is a scanning exposure of near-infrared  
radiation

16. The method of claim 14, wherein said  
exposing is a blanket exposure of near-infrared  
radiation through a mask.

10 17. The method of claim 14, wherein said  
exposing is a scanning exposure of near-ultraviolet  
radiation through a mask.

15 18. The method of claim 14, wherein said  
exposing is a blanket exposure of near ultraviolet  
radiation.

19. The method of claim 14 further comprising:  
exposing said recording element with  
near-infrared radiation to read the a color density or  
hue shift.

20 20. The method of claim 14, wherein said  
optical recording element further comprising:  
a polymeric binder.

21. The method of claim 14, wherein said  
optical recording element further comprises:

25 a near-ultraviolet absorbing sensitizer.

22. The method of claim 21, wherein said  
exposing is a scanning exposure of near-ultraviolet  
radiation.

23. The method of claim 21, wherein said  
30 exposing is a blanket exposure of near-ultraviolet  
radiation.

24. An optical recording element comprising:  
a reflective substrate and  
a recording layer coated on said substrate  
35 comprising:  
a near-infrared absorbing dye chosen from

- 27 -

the group consisting of cyanines which undergoes a color density or hue shift following exposure of said recording layer with near-infrared radiation;

5 an acid-photogenerating compound chosen from the group consisting of aryl halonium salts, aryl phosphonium salts aryl arsenonium salts, aryl sulfonium salts, aryl selenonium salts, aryl diazonium salts, and mixtures thereof;

10 a near-ultraviolet absorbing sensitizer chosen from the group consisting of xanthones, indandiones, indanones, throxanthones, acetophenones, benzophenones, anthracenes, dialkoxyanthracenes, perylenes, phenothiazenes, and pyrenes; and

15 a polymeric binder.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/07635

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1. 5 G11B7/24		
II. FIELDS SEARCHED		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.C1. 5	G11B ; C03C ; G03G	
Documentation Searched other than Minimum Documentation <sup>8</sup> to the Extent that such Documents are Included in the Fields Searched <sup>9</sup>		
III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>10</sup>		
Category <sup>11</sup>	Citation of Document <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	FR,A,2 139 725 (KODAK-PATHÉ) 12 January 1973 see claims 1,8 ---	1,2
X	DE,A,2 043 769 (ITEK CORP.) 4 March 1971 see claims 1,2 ---	1,2
A	EP,A,0 244 704 (EASTMAN KODAK) 11 November 1987 cited in the application * CLAIMS * ---	1
A	EP,A,0 278 763 (CANON) 17 August 1988 * CLAIMS * ---	1-24 -/-
<p>* Special categories of cited documents :<sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"T" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"a" document member of the same parent family</p>		
IV. CERTIFICATION		
1	Date of the Actual Completion of the International Search 01 DECEMBER 1992	Date of Mailing of this International Search Report 07.12.92
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer VOGTT C. C. Vogg

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Character of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 302 610 (3M) 8 February 1989 * CLAIMS *	1
A	EP,A,0 120 601 (3M) 3 October 1984 see page 16, paragraph 5; claims 1-14	1
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 332 (P-1077) 17 July 1990 & JP,A,21 11 946 ( KONICA ) 24 April 1990 see abstract	1
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 75 (P-831) 21 February 1989 & JP,A,63 261 352 ( FUJI PHOTO ) 28 October 1988 see abstract	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. US 9207635  
SA 64566

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 01/12/92

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